California Environmental Protection Agency

Air Resources Board

SOP MLD064

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF ANIONS AND CATIONS IN PM $_{2.5}$ SPECIATION SAMPLES BY ION CHROMATOGRAPHY

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1 Introduction

In 1997, the U.S. Environmental Protection Agency created new federal air quality standards for $PM_{2.5}$ and ozone, and proposed new requirements to reduce the regional haze that impairs visibility. The $PM_{2.5}$ standards complement existing federal and state standards that target the full range of inhalable particulate matter (PM_{10}). Efforts to characterize PM $_{2.5}$ and comply with the federal standards will further progress toward California's own PM_{10} standards.

The goal of the $PM_{2.5}$ monitoring program is to provide ambient data that support the nation's air quality programs. These data include mass measurements and chemically resolved, or speciated data. Mass measurements are used principally for comparison to the $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS). These comparisons identify areas that do or do not meet the $PM_{2.5}$ NAAQS, thereby allowing areas to be designated as attainment or nonattainment. Speciated data support the development of emission mitigation strategies intended to reduce ambient $PM_{2.5}$ levels. The data are used to evaluate emissions inventory and air quality models, analyze source attribution, and track the success of emission control programs.

2 Summary of Method

Method MLD064 determines anions (nitrate and sulfate) and cations (sodium, ammonium, and potassium) collected on nylon filters exposed to ambient air, which are submitted to the laboratory by site operators. The filters are extracted in deionized water by sonicating for one hour, shaking for one hour, and storing overnight in a refrigerator. The extract is analyzed by ion chromatography using a system comprised of a guard column, analytical column, a self regenerating suppressor, and a conductivity detector. Peak analysis is determined using Dionex Peaknet Chromatography Workstation software, version 6.40.

3 Interferences and Limitations

3.1 Co-elution interference can be caused by ions with retention times that are similar to and thus overlap those of the ions of interest, or by large amounts of any one anion or cation that interferes with the peak resolution of an ion with closely matching retention time. Sample dilution or a decrease in eluant concentration can reduce these co-elution interferences.

3.2 Interferences may be caused by contaminants in the reagent water, reagents, glassware, nylon filters, and other sample processing apparatus that could lead to an elevated baseline or detectable concentrations of any of the ions of interest. A reagent water blank, extraction water blank, and a filter blank are run with each set of samples to monitor these possible sources of contamination.

3.3 Losses in retention time and resolution can be signs of column deterioration. Monitoring analyte retention times and column back pressure will assist in determining when a column or guard column may need to be replaced.

4 Instrument and Equipment

This SOP assumes familiarity with the installation and operation of the Dionex Ion Chromatographic system (IC). For detailed instructions in the operation of the Dionex IC, refer to the Dionex operations manual.

4.1 The Dionex IC is comprised of modular units purchased from the Dionex Corporation, one of each of the following for Anions and one for Cations:

1. Gradient pump
2. Chromatography Enclosure (shared by both anions and cations)
3. Conductivity detector
4. Automated sampler

4.2 IC Operating conditions:

Sample loop volume	100µL for Anions and Cations
Analytical columns: Anions Cations	 Dionex, IonPac AS4A Dionex, IonPac CS12A
Guard columns: Anions Cations	 Dionex, IonPac AG4A Dionex, IonPac CG12A
Eluent solutions: Anions Cations	 1.5 mM carbonate / 1.7 mM bicarbonate 20 mM Methanesulfonic Acid
Eluent flow rates: Anions Cations	 2.0 mL / minute 1.0 mL / minute
Acquisition Software	Dionex Peaknet Chromatography Workstation software, version 6.40.

4.3 Other Equipment:

1. Bottle-top dispenser, 25.0 mL volume
2. Analytical balance
3. Pipettor with disposable pipette tips: 50 – 1000 μL and 100 – 5000 μL
4. Ultrasonicator
5. Shaker table

5 Materials and Chemicals

5.1 Materials:

1. Volumetric flasks: 100, 250, 500, and 1000 mL sizes
2. Polyethylene storage bottles: 125, 250, 500, and 1000 mL sizes
3. Plastic centrifuge tubes with caps, 50 mL size
4. Dionex 5 mL autosampler vials with 20 μm filter caps
5. Beaker, 1 L size
6. High purity helium
7. High purity nitrogen
8. Gloves, disposable, class 100

5.2 Chemicals: All chemicals are at least spectrophotometric grade.

1. Sodium bicarbonate ($NaHCO_3$)
2. Sodium carbonate (Na_2CO_3)
3. Methanesulfonic Acid (CH_3SO_2OH)
4. Nanopure ASTM Type 1 deionized water (>16 MΩ-cm)

5.3 Anion and Cation stocks are National Institute of Science and Technology (NIST) traceable. Two stock solutions of each are purchased, one for making working standards, the other for making a working control. The two solutions are of different sources, whether they are from different lot numbers or different companies.

6 Preparation of Eluents

6.1 Stock eluents are prepared in nanopure water. The following table lists the amounts of each chemical used to make one batch of stock solution.

Stock Eluant	Amount per Batch
Anions: Sodium carbonate / sodium bicarbonate	 600 mM (15.90 g/250 mL) / 680 mM (14.28 g/250 mL)
Cations: Methanesulfonic acid (MSA)	 1.0 M (96.10 g/L)

6.1.1 Anion eluant stock: Weigh the sodium carbonate and sodium bicarbonate into a 1L beaker containing a magnetic stir bar. Add approximately 150mL nanopure deionized water and dissolve while stirring on a magnetic stirrer. Once all chemicals have dissolved, transfer eluent stock to a 250 mL volumetric flask and bring to volume with nanopure deionized water. Transfer to a polyethylene storage bottle and store in the refrigerator. The stock solution may be stored for up to one year and then must be remade.

6.1.2 Cation eluant stock: Weigh the MSA into a 1L beaker containing a magnetic stir bar. Add approximately 700 mL nanopure deionized water. Mix thoroughly using a magnetic stirer, allow to cool, transfer to a 1L volumetric flask and bring to volume with nanopure deionized water. Transfer to a polyethylene bottle and store in the refrigerator. The stock solution may be stored for up to one year and then must be remade.

6.2 The working eluents are prepared by diluting the eluent stocks.

6.2.1 Anion working eluant (1.5 mM Na_2CO_3 / 1.7 mM $NaHCO_3$) Add 20.0mL of anion stock eluant to an 8L carboy and bring to volume with nanopure deionized water. Mix well and transfer to the eluant reservoirs on the IC.

6.2.2 Cation working eluant (20 mM MSA): Add 160 mL of cation stock eluant to an 8L carboy and bring to volume with nanopure deionized water. Mix well and transfer to the eluant reservoirs on the IC.

7 Preparation of Anion and Cation Standards and Controls

The anion standard and control stock solutions are both 1000μg/mL and the cation standard and control stock solutions are both 500μg/mL. All standard and control solutions are stored in the refrigerator until ready for use.

7.1 Anion working standards: The following table lists the dilutions used to prepare the working standards for anion analysis. All dilutions are made using nanopure deionized water. Store the working standards in polyethylene bottles in the refrigerator. Working standards are usable for no more than 21 days before they must be prepared again from the stock solution.

Final Concentration (μg/mL)	Final Dilution Volume (mL)	Stock Concentration (μg/mL)	Volume of Stock Solution Needed (mL)
0.02	100	20	0.100
0.05	100	20	0.250
0.10	100	20	0.500
0.20	100	20	1.000
0.50	250	1000	0.125
1.0	100	1000	0.100
2.0	100	1000	0.200
5.0	100	1000	0.500
10.0	100	1000	1.00
20.0	100	1000	2.00

7.2 Cation working standards: The following table lists the dilutions used to prepare the working standards for cation analysis. All dilutions are made using nanopure deionized water. Store the working standards in polyethylene bottles in the refrigerator. Working standards are usable for no more than 21 days before they must be prepared again from the stock solution.

Final Concentration (μg/mL)	Final Dilution Volume (mL)	Stock Concentration (μg/mL)	Volume of Stock Solution Needed (mL)
0.02	100	20	0.100
0.05	100	20	0.250
0.10	100	20	0.500
0.20	100	20	1.000
0.50	250	500	0.250
1.0	100	500	0.200
2.0	100	500	0.400
5.0	100	500	1.000
20.0	100	500	4.000

7.3 Controls: The anion and cation controls are prepared from a secondary source stock. The control concentration is 0.500 μg/mL and is prepared using the same dilutions as used to prepare the 0.500 μg/mL anion and cation standards. All dilutions are made using nanopure deionized water. Store the controls in polyethylene bottles in the refrigerator. Controls are usable for no more than 21 days before they must be prepared again from the stock solution.

8 Filter Analysis

Nylon filter samples are stored in a refrigerator at 4 ^{o}C until analysis.

8.1 Prepare a worklist of samples to be analyzed and the analyze by date. Ion samples must be analyzed within 20 business days after receipt in the laboratory.

8.2 Prepare a sequence for the analytical run that begins with the calibration standards in order of increasing concentration, followed by a water blank, a control and a check standard. Follow these with the list of samples, including at least 10% duplicates and, after each 10 analyses, another check standard. At the end of the samples, an extraction water blank, a filter blank, and a spike are analyzed. The last analysis of each run is another check standard.

8.3 Filters are received for ion analysis contained in 50 mL plastic centrifuge tubes. Label four additional centrifuge tubes as extraction water blank, filter blank, anion spike, and cation spike. Place a new, cleaned nylon filter in the filter blank, anion spike, and cation spike tubes. Add 25.0 mL nanopure deionized water to all tubes. To the anion and cation spike tubes also add 0.641 mL of the 20 μg/mL anion and cation working standard, respectively.

8.4 Securely replace the lids on each centrifuge tube, place them in a rack inside of the Ultrasonicator and fill with tap water to the fill line. Turn on the sonication function for 60 minutes.

8.5 After 60 minutes of sonication, remove the samples from the ultrasonicator, drain on a towel, and place them on the shaker table. Set the timer for 60 minutes.

8.6 After shaking for 60 minutes, remove the samples from the shaker table and store in the refrigerator at 4 ^{o}C overnight. The samples are now ready for IC analysis.

8.7 Transfer approximately 5 mL of working standards, controls, check standards, blanks, and extracted samples to Dionex IC autosampler vials in an autosampler cartridge. Samples that are to be analyzed in duplicate use only 3 mL for both the original and the duplicate aliquot to conserve sample extract for possible dilutions or reanalysis. Cap each vial with a filter cap. Place the cartridges on the autosampler and begin the analysis. The remaining portions of the extracts are stored refrigerated for 6 months after analysis.

9 Quality Control

9.1 The LOD is described as the lowest concentration an analyst can quantify with a certain confidence level. The calculated limit of detection for the method is determined by analyzing a low standard seven times according to 40 CFR, Appendix B, as follows:

$$\mathrm{LOD} = T_{(n-1,1-\alpha=0.99)}(\mathrm{sd})$$

where (sd) is the standard deviation and is calculated for the seven replicates. The published LOD is based on the calculated LOD and the chemist's experience of the method and instrument and takes into account variation of instrument performance over time. An annual check of the LOD verifies that the published LOD remains acceptable. The table below lists the current verified and published LOD values. The verified LOD = 3.143 x standard deviation and the published LOD = 10 x standard deviation. Verified and published LOD values are rounded off to the nearest hundredth (0.01) μg/mL. The standard used for the new LOD determination must be between the old verified LOD and five times the old verified LOD and the new verified LOD must be less than the published LOD.

	Nitrate	Sulfate	Sodium	Ammonium	Potassium
Low Standard Used	0.02	0.05	0.02	0.02	0.07
Standard Deviation	0.0024	0.0066	0.0033	0.0018	0.0052
Verified LOD	0.01	0.02	0.01	0.01	0.02
Published LOD	0.02	0.07	0.03	0.02	0.05

(All units are in μg/mL)

9.2 Ten standards are analyzed for the anion calibration curve and eight standards for the cation calibration curve. In order for the calibration curve to be acceptable, the correlation coefficient must be greater than or equal to 0.990. If the correlation coefficient is less than 0.990, the standards are re-analyzed.

9.3 A control is analyzed after the calibration is complete. The acceptable limits for the control are determined annually using results of control analysis over the previous year. The limits are defined as follows:

Upper Control Limit (UCL)= average value + 3 times the standard deviation
Upper Warning Limit (UWL)= average value + 2 times the standard deviation
Lower Warning Limit (LWL)= average value - 2 times the standard deviation
Lower Control Limit (LCL)= average value - 3 times the standard deviation

The initial values for control limits were calculated from results of analysis over the first six months of the program. These values are shown in the table below as an example of the ranges to be expected.

	Nitrate	Sulfate	Sodium	Ammonium	Potassium
Number of controls	12	12	14	14	13
Standard Deviation	0.0119	0.0170	0.0151	0.0094	0.0105
UCL	0.507	0.544	0.546	0.548	0.523
UWL	0.495	0.527	0.531	0.539	0.512
Average	0.471	0.493	0.501	0.520	0.491
LWL	0.447	0.459	0.471	0.501	0.470
LCL	0.436	0.442	0.456	0.492	0.460

(All units are in μg/mL)

If the control value is out of the acceptable limits, the instrument is evaluated for problems and a control reanalyzed successfully before samples are analyzed.

9.4 The check standard is analyzed before any samples, again after each group of ten analyses, and finally at the end of the analysis. The acceptable limits for the check standards are determined in the same manner as for the control, using results of check standard analysis over the previous year. The initial values for check standard limits were calculated from results of analysis over the first six months of the program. These values are shown in the table below as an example of the ranges to be expected.

	Nitrate	Sulfate	Sodium	Ammonium	Potassium
Number of check standards	55	55	55	55	52
Standard Deviation	0.0139	0.0160	0.0183	0.0062	0.0105
UCL	0.515	0.536	0.568	0.546	0.534
UWL	0.501	0.520	0.550	0.540	0.523
Average	0.473	0.488	0.513	0.527	0.502
LWL	0.446	0.456	0.477	0.515	0.481
LCL	0.432	0.440	0.458	0.509	0.471

(All units are in μg/mL)

9.5 If the check standard is not within acceptable limits, the instrument is evaluated for problems and a control sample is reanalyzed successfully before samples are analyzed.

9.6 Nanopure deionized water blanks, extraction water blanks, and filter blanks are analyzed with each set of extracted filters. Blank levels are monitored to assure that contamination from reagents or from sampling processing techniques are not affecting sample results

9.7 Spikes are run to measure the accuracy of the entire sampling handling process. Spikes are prepared from unexposed filters and extraction water with an amount of standard added to bring the final extract concentration to an expected value of 0.500 μg/mL. A spike is extracted and analyzed with each sample set. The spike recovery limit is 100% ± 20% (0.400 – 0.600 μg/mL).

9.8 Duplicates are run at a frequency of at least 10% and consist of a separate aliquot of the filter extract. The % difference between duplicates should be less than 10% for samples whose concentration is more than twenty times above the LOD, and less than 25% for samples whose concentration is less than twenty times the LOD.

10 References

1. Method 300.6, Othophosphate, Nitrate, and Sulfate in Wet Deposition by Chemically Suppressed Ion Chromatography, USEPA, March 1986.

2. Quality Assurance Guidance Document, Final, Quality Assurance Project Plan, PM 2.5 Speciation Trends Network Field Sampling, EPA-4154/R-01-001.